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Aging Studies of Filled and Unfilled VCE

S. Letant, C. Alviso, M. Pearson, T. Wilson, S. Chinn, R. Maxwell

April 7, 2011

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Aging Studies of Filled and Unfilled VCE

Sonia E. Létant, Cynthia T. Alviso, Mark Pearson, Thomas S. Wilson, Sarah C. Chinn, and Robert S. Maxwell

Abstract

VCE is an ethylene, vinyl acetate, vinyl alcohol elastomer used to bind high volumes of micro-particles. Surveillance data for this material is both scarce and scattered, complicating the assessment of any aging trends in systems. In addition, most of the initial surveillance efforts focused on mechanical properties such as hardness and tensile strength, and chemical information is therefore lacking. The initial work conducted in FY09 focused on the effects of gamma radiation up to 25 MR on filled and unfilled VCE material produced by the Kansas City Plant (KCP) using WR-qualified processes. The work performed in FY10 focused on the effects of temperatures up to 150°C on the VCE material produced by KCP, as well as on a comprehensive data integration to generate a mechanistic understanding of degradation mechanisms in the VCE material. A series of structural and chemical characterization techniques were employed including: Toluene Swelling, Tensile Testing, Solid Phase Micro Extraction – Gas Chromatography – Mass Spectrometry, Infra-Red Spectroscopy, and UV-vis Spectroscopy. Overall results from FY09 and FY10 show a ‘yellowing’ of the material, an increased release of acetic acid and an increased Young’s modulus with increased temperature and increased gamma irradiation dose. When subjected to gamma radiation, VCE samples also showed increased cross-linking, reduced mobility, and hindered IR deformation modes. These observations may be explained by a model in which acetic acid is eliminated from the vinyl acetate group via a molecular rearrangement in which a Hydrogen atom from the ethylene backbone moves to the acetate group. This mechanism releases acetic acid and forms a C=C double bond in the polymer backbone, therefore reducing chain mobility, hindering ethylene deformation modes, affecting the mechanical properties of the VCE material and generating a yellow color through the formation of polyenes. The work showed that acetic acid may constitute an effective chemical signature to probe the aging of VCE material in systems. Future efforts will involve work with actual VCE parts to develop a comprehensive aging model of VCE in systems.

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1. Introduction

VCE is an ethylene/vinyl acetate/vinyl alcohol terpolymer binder for filled elastomers (Figure 1) which is designed to accept high filler loadings. Filled elastomer parts consist of the binder (VCE), a curing agent (Hylene MP, diphenol-4,4'-methylenebis(phenylcarbamate)), a processing aid (LS, lithium stearate), and filler particles (typically 70% fraction by weight). The curing of the filled elastomer parts occurs from the heat-activated reaction between the hydroxyl groups of VCE with the Hylene MP curing agent, resulting in a cross-linked network (Figure 2). The final vinyl acetate content is between 34.9 and 37.9%, while the vinyl alcohol content is between 1.27 and 1.78%.

Surveillance data for this material is both scarce and scattered, complicating the assessment of any aging trends in systems. In addition, most of the initial surveillance efforts focused on mechanical properties such as hardness and tensile strength, and chemical information is therefore lacking.

Material characterization and aging studies had been performed on previous formulations of the VCE material [1-2] but the Ethylene Vinyl Acetate (EVA) starting copolymer is no longer commercially available. New formulations with replacement EVA materials are currently being established and will require characterization as well as updated aging models [3, 4].

The initial work conducted in FY09 focused on the effects of gamma radiation up to 25 MR on the chemical and structural properties of filled and unfilled VCE material synthesized, milled, molded and cured by the Kansas City Plant (KCP) using WR-qualified processes (see KCP-613-6051), as well as initial results with thermally-aged samples. The work performed in FY10 and presented in this report focuses on the effects of temperatures up to 150°C on the VCE material produced by KCP, and on additional measurements on samples exposed to gamma radiation. A comprehensive data integration was also performed in order to generate a mechanistic understanding of degradation mechanisms in the VCE material, which sparked a collaboration with David Plant and Mark Read at AWE, who are using Density Functional Theory (DFT) to calculate the lowest energy configurations of a similar polymer used in the UK, as well as corresponding IR spectra. A manuscript is in preparation, to be submitted to the Journal of Polymer Degradation in a few months.

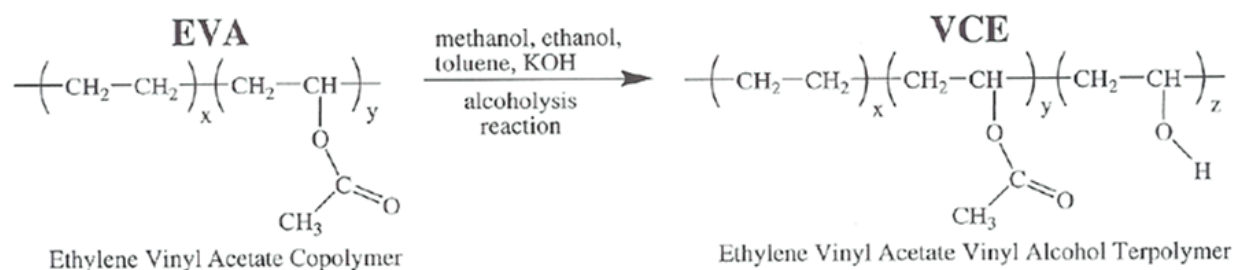


Figure 1: Base-catalyzed alcoholysis reaction of EVA copolymer yielding VCE [3]. Typical VCE composition is 34.9-37.9% vinyl acetate, and 1.27-1.78% hydroxyl.

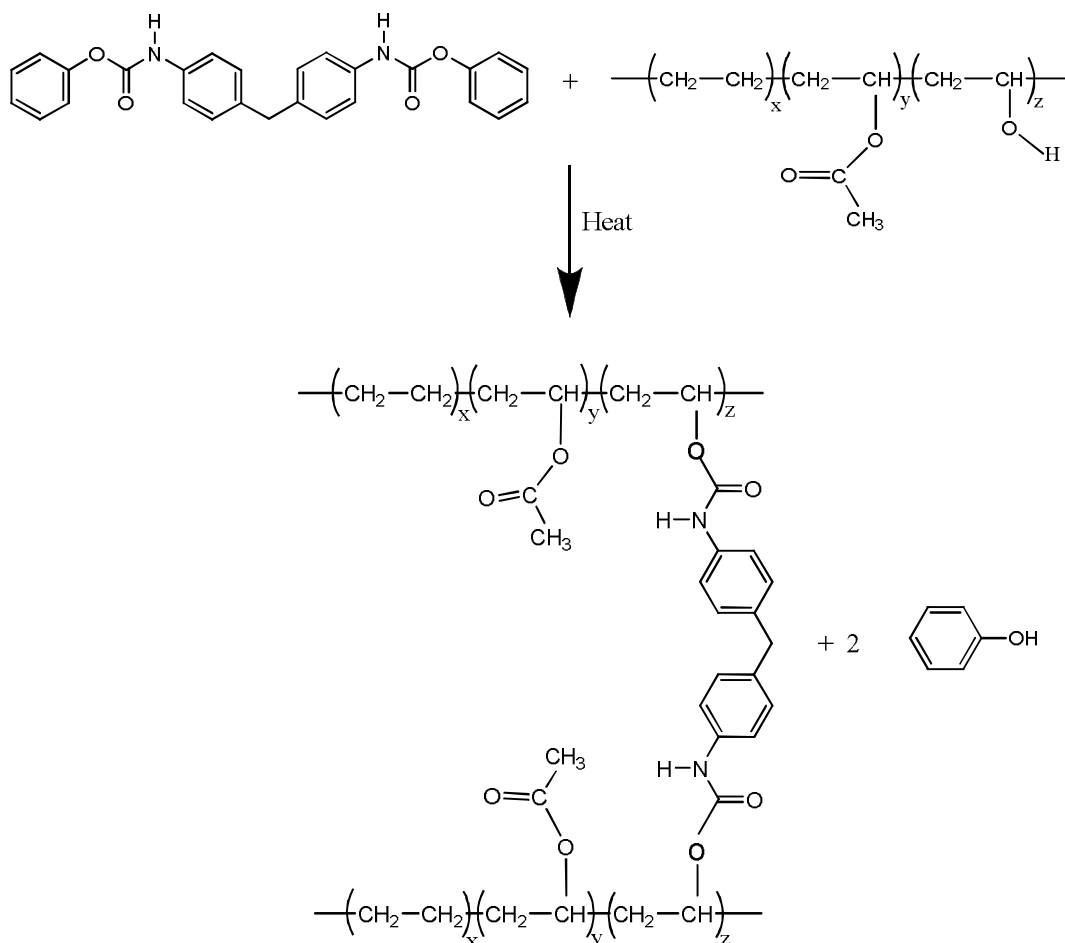


Figure 2: Curing reaction between VCE and Hylene MP [3].

2. Experimental Approach

2.1. Sample preparation

VCE samples were synthesized via alcoholysis of EVA in the presence of sodium hydroxide. The material used in this study was custom-synthesized at Honeywell Federal Manufacturing & Technologies, Kansas City, MO, with a vinyl alcohol content of 1.5 % and a vinyl acetate content of 35 %. After blending with 10 % diphenol-4-4',-methylenabis(phenylcarbamate) and 1-2% lithium stearate (used as a lubricant) on a 2-roll mill, the VCE material was injected in molds and cured at 179°C for 30 min, resulting in the cross-linked network shown in Figure 2. Phenol released during the cross-linking reaction was removed using a thermal post-cure treatment at 120°C for 5 hr.

VCE sheets with a diameter of 11” and a thickness of 0.030” were checked for uniformity using X-ray radiography and packaged with desiccant and heat-sealed sleeves prior to shipping to LLNL.

Identical samples were maintained in dry conditions, sealed into plastic bags, placed into a stainless steel vessel and exposed to a 1.2 MeV, 5 kGray/hour, ⁶⁰Co gamma-ray source. The final gamma irradiation doses generated for this study were 10 kGray (1 MRad) and 250 kGray (25

MRad) respectively. A set of samples was also thermally aged for 24 hr at 50, 100, 125, 150, 175, 200, 250 and 300 °C respectively, using a muffle furnace. Another set of samples was thermally aged under inert conditions at 20, 70 and 150°C, and held at these respective temperatures for 1 and 7 months respectively. Degraded samples were analyzed alongside pristine samples.

2.2. Solid Phase Micro Extraction – Gas Chromatography / Mass Spectrometry (SPME-GC/MS)

VCE samples (20-30 mg each) were placed in 20 mL SPME headspace glass vials, and sealed under nitrogen with crimp caps and septa (20 mm, Teflon/blue silicone, level 4, MicroLiter Analytical Supplies Inc., Suwanee, GA).

For radiation-aged samples, and samples aged in the muffle furnace, 5 replicates were left at room temperature and another 5 replicates were placed in an oven at 150°C. All samples remained at their designated temperatures for two weeks. An additional set of references (sealed empty vials) was also prepared for storage at room temperature and 150°C prior to SPME sampling. The storage at elevated temperatures was performed to maximize the volatilization of degradation signatures for observation by SPME sampling, while retaining room temperature samples and blanks to serve as controls.

For the holding study, 5 VCE samples were held at 20°C, 15 samples were held at 70°C, and 15 samples were held at 150°C. Five samples were analyzed after 2 weeks, 5 samples were analyzed after 1 month, and the last 5 samples were analyzed after 7 months.

Samples were analyzed by SPME-GC-MS using an automated GC-MS system (GC model 6890 and MS model 5973, both from Agilent Technologies Inc., Santa Clara, CA) with the following conditions: 85 µm Carboxen/Polydimethylsiloxane SPME fiber (Sigma-Aldrich Inc., St. Louis, MO), conditioned between samples for 5 min at 260 °C. Each vial headspace was sampled at 50°C for 20 min and injected into the GC for 1 min at 250°C. The GC was set for ‘splitless’ injection and purged for 0.5 min with a constant 1.0 mL/min flow of helium. The column used for these experiments was designed for volatile analysis (30 m, 0.25 mm ID, 1.4 µm film, DB-624, Agilent Technologies Inc., Santa Clara, CA). Each 20 min run had the following temperature profile: 40°C hold for 1.05 min, 23.41°C /min ramp to 260°C, and 260°C hold for 6.81 min. The MS scanned the mass range from 35-450 m/z at a rate of 1.81 scans/s without filament delay. Materials outgassing from the VCE samples were identified by comparison of their mass spectra to the NIST 02 mass spectral library.

2.3. Toluene Swelling

VCE samples were cut into pieces weighing approximately 150 mg. Each piece was weighed with mg precision before being placed into a 40 mL glass vial and submerged with toluene. Vials were sealed and samples were let to swell for 24 hr. The next day, samples were removed from the vial, quickly dried with absorbent paper, and weighed a second time. Three replicates were analyzed for each set of experimental conditions.

2.4. Tensile testing

Mechanical measurements were made on an Instron (Model 5500-R) using a 10 lb load cell equipped with pneumatic grips. Test samples were cut from the pristine or aged material to ASTM D-638 Type V dogbones using a punch. Materials were assumed to have a nominal thickness of 30 mils (0.762 mm). Testing was performed using a grip separation of 25.4 mm,

which was used as the gage length for all calculations. For each sample (material/preparation condition), 5 specimens (replicates) were tested to failure at a crosshead speed of 0.5 in/minute.

2.4. Infra-Red spectroscopy

Infra-red spectra were acquired using a Bruker Hyperion spectrometer fitted with a 20X Attenuated Total Reflectance (ATR) objective, and a pressure setting of 3 (out of 5). All the spectra presented in this report were acquired using the same settings. Five replicate samples were analyzed for each set of experimental conditions and representative spectra are presented (there were generally no statistical differences between replicate spectra).

3. Results and Discussion

3.1. Solid Phase Micro Extraction – Gas Chromatography / Mass Spectrometry (SPME-GC/MS)

SPME-GC/MS experiments were performed on gamma-irradiated samples held at room temperature, and on a duplicate sample set held at 150°C (storage at elevated temperatures was performed in order to maximize the volatilization of degradation products). Figure 3 shows GC-MS spectra of unfilled VCE samples exposed to various doses of radiation before being held in vials for 2 weeks at 150°C. The main outgassing chemicals identified were: silanol, acetic acid, butanoic acid, propanoic acid, and phenol (ranked according to their retention times).

The main peak, identified as acetic acid according to the NIST 02 mass spectrometry library, was confirmed by performing SPME-GS-MS on a vial spiked with acetic acid (identical retention times were obtained). Although the method is not quantitative, integrated peak areas are reported for acetic acid in Table 1, to provide a qualitative indication of the effects of temperature and irradiation on the outgassing of acetic acid from the VCE material. This approach relied on the fact that all samples were analyzed in a single batch, without tuning the instrument between samples. As seen in Table 1, no acetic acid evolution was observed at room temperature without irradiation, but the release of this chemical qualitatively increased with both temperature and irradiation independently.

In another study, filled VCE samples were held under inert atmosphere in SPME-GC-MS vials at 20, 70 and 150°C for 1 and 7 months respectively. The corresponding data, presented in Table 2, showed no significant outgassing at room temperature. The amount of acetic acid outgassed from the samples increased with temperature, but at a fixed temperature the acetic release appeared to plateau after 1 month, indicating that most of the outgassing occurred during the first weeks of thermal aging. Again, it should be noted that SPME-GC-MS is not a quantitative technique and that these observations are mostly qualitative.

Propanoic and butanoic acids were detected in low abundance at high temperature and/or high gamma irradiation doses and may be fragments of the lithium stearate processing aid. Phenol, also detected in low abundance, is a degradation product of the crosslinking agent (see Scheme 1) used in the synthesis of VCE, resulting from thermal unblocking of urethane. Finally, the presence of low concentrations of silanol was attributed to the outgassing of silicone used for mold release during the curing of the VCE samples

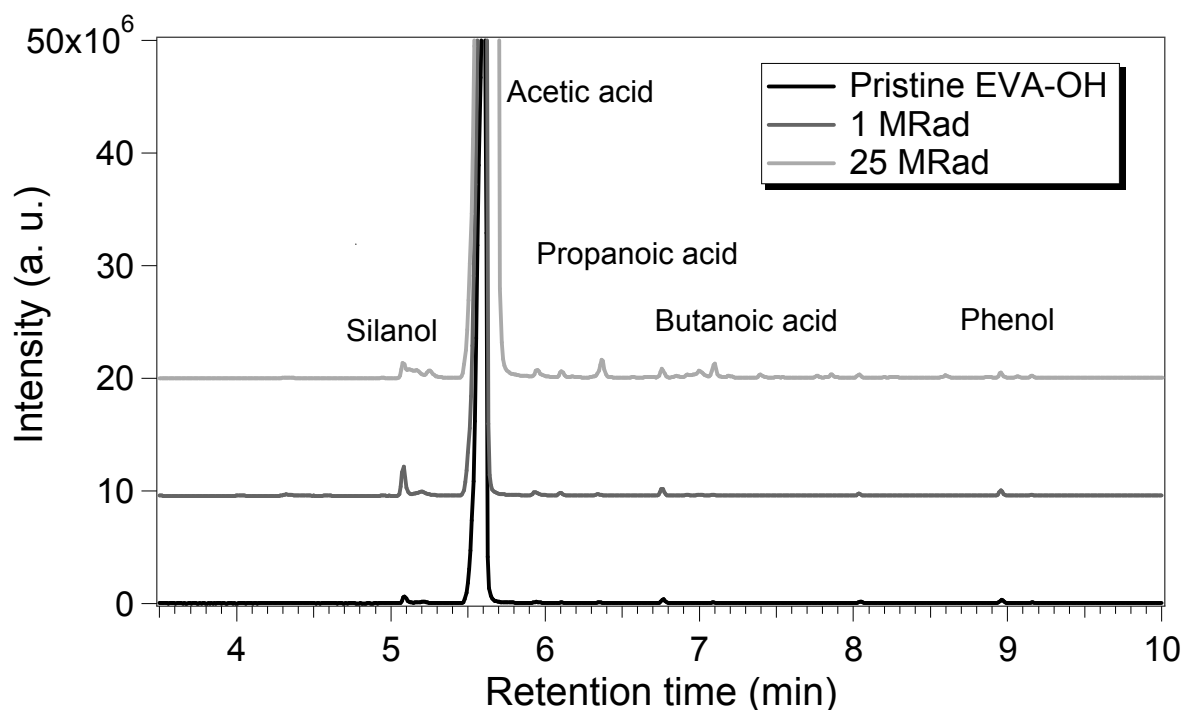


Figure 3. SPME-GC/MS total ion chromatogram of the headspace of vials containing VCE samples exposed to gamma irradiation doses of 0, 1 and 25 MRad. Samples were held at a constant temperature of 150°C for 2 weeks.

Table 1. SPME-GC/MS analysis of acetic acid evolution from unfilled VCE samples exposed to thermal degradation at 150°C and gamma irradiation doses of 0, 1 and 25 MRad. Total ion chromatogram peak areas are reported for each set of experimental conditions. Results from 5 replicate samples were averaged and corresponding standard deviations are provided.

Experimental Conditions	Gamma Irradiation Dose (MRad)	0		1		25	
	Thermal Aging Temperature (°C)	20	150	20	150	20	150
Acetic acid outgassing	Acetic acid peak area (a. u.)	0	$2.2 \cdot 10^9$	$1.5 \cdot 10^7$	$2.8 \cdot 10^9$	$1.2 \cdot 10^9$	$5.8 \cdot 10^9$
	Standard deviation (a. u.)	0	$6.0 \cdot 10^8$	$5.0 \cdot 10^6$	$7.0 \cdot 10^8$	$2.0 \cdot 10^8$	$7.0 \cdot 10^8$

Table 2. SPME-GC/MS analysis of acetic acid evolution from filled VCE samples exposed to thermal degradation at 20, 70 and 150°C for 1 and 7 months, under inert atmosphere. Total ion chromatogram peak areas are reported for each set of experimental conditions. Results from 5 replicate samples were averaged and corresponding standard deviations are provided.

Experimental Conditions	Thermal Aging Temperature (°C)	20		70		150	
	Time (months)	1	7	1	7	1	7
Acetic acid outgassing	Acetic acid peak area (a. u.)	0	0	$1.0 \cdot 10^7$	$7.0 \cdot 10^6$	$1.4 \cdot 10^{9*}$	$1.8 \cdot 10^{9*}$
	Standard deviation (a. u.)	0	0	$5.0 \cdot 10^6$	$1.8 \cdot 10^6$	$4.0 \cdot 10^8$	$1.0 \cdot 10^9$

*Saturation of the acetic acid peak is observed on some of the spectra.

3.2. Toluene Swelling

Toluene swelling experiments were performed in order to assess the level of cross-linking in the VCE material. A slight decrease in swell ratio was measured for irradiated samples (see Table 3), which is attributed to an increased cross-linking upon radical formation in the material. No statistical difference was observed on thermally-treated samples (see Table 4), indicating no significant change in the cross-linking of the material upon thermal aging.

Table 3. Toluene swell ratio (V/V_0) of filled and unfilled VCE samples exposed to gamma irradiation doses of 0, 1 and 25 MRad. W_2/W_1 is the ratio of the masses of the swollen and dry EVA-OH materials. The swell ratio $V/V_0 = 1.314 (W_2/W_1) - 0.314$. Each value represents the average of 3 replicate samples.

Filler	Gamma Irradiation Dose (MRad)	Swell Ratio (V/V_0)	Standard Deviation
Unfilled	0	5.11	0.03
	1	5.07	0.09
	25	4.52	0.01
Filled	0	3.00	0.01
	1	2.69	0.01
	25	2.60	0.03

Table 4. Toluene swell ratio (V/V_0) of filled VCE samples exposed to temperatures of 20, 70 and 150°C for 1 month under inert atmosphere. W_2/W_1 is the ratio of the masses of the swollen and dry EVA-OH materials. The swell ratio $V/V_0 = 1.314 (W_2/W_1) - 0.314$. Each value represents the average of 3 replicate samples.

Filler	Thermal treatment	Swell Ratio (V/V_0)	Standard Deviation
Filled	1 month 20°C	3.00	0.01
	1 month at 70°C	3.00	0.01
	1 month at 150°C	3.07	0.02

3.3. Tensile testing

Tensile testing performed on gamma-irradiated VCE samples showed no statistical difference between pristine and irradiated samples for unfilled material, but filled VCE samples showed a decrease in tensile strength and an increase in Young's modulus upon gamma irradiation (see Table 5).

Tensile testing performed on thermally aged, filled VCE samples showed a significant increase in both tensile strength and Young's modulus upon thermal aging after 1 and 7 months (see Tables 6 and 7). It should be noted that no mechanical measurements were performed on samples aged for 7 months at 150°C. These samples were distorted and too brittle to handle.

Table 5. Mechanical properties of filled and unfilled VCE samples exposed to gamma irradiation doses of 0, 1 and 25 MRad. Results from 5 replicates were averaged and standard deviations are provided.

Samples	Gamma Irradiation (MR)	Tensile strength (psi)	Young's modulus (psi)
Unfilled VCE	0	697 ± 207	680 ± 27
	1	887 ± 74	661 ± 26
	25	822 ± 138	691 ± 17
Filled VCE	0	1183 ± 41	10971 ± 679
	1	1112 ± 22	10872 ± 890
	25	1079 ± 15	12205 ± 578

Table 6. Mechanical properties of filled VCE samples exposed to temperatures of 20, 70 and 150°C for 1 month under inert atmosphere. Results from 5 replicates were averaged and standard deviations are provided.

Samples	Thermal treatment (°C)	Tensile strength (psi)	Young's modulus (psi)
Filled VCE	1 month 20°C	1183 ± 41	10971 ± 679
	1 month at 70°C	1216 ± 49	13879 ± 605
	1 month at 150°C	1301 ± 46	15994 ± 863

Table 7. Mechanical properties of filled VCE samples exposed to temperatures of 20, 70 and 150°C for 7 months under inert atmosphere. Results from 5 replicates were averaged and standard deviations are provided.

Samples	Thermal treatment (°C)	Tensile strength (psi)	Young's modulus (psi)
Filled VCE	7 month 20°C	1183 ± 41	10971 ± 679
	7 month at 70°C	1102 ± 35	13192 ± 1128
	7 month at 150°C	Sample too brittle	Sample too brittle

3.4. Infra-Red spectroscopy

IR absorption spectra recorded with an ATR system showed no significant changes in the overall structure of the VCE material after gamma irradiation (see Figure 4). Peaks were indexed as follows: (1) stretching and bending modes from vinyl acetate groups, (2) stretching modes from vinyl alcohol groups, (3) stretching modes from methylene backbone, (4) deformation modes from methylene backbone, (5) bending modes from aromatic groups, and (6) stretching modes from C=C and C=O bonds. While most of the peaks remained unchanged after gamma irradiation, one of the methylene backbone deformation modes, centered at 1460 cm⁻¹, was significantly hindered after exposure to gamma irradiation for the unfilled VCE material, which is consistent with a decreased mobility of the methylene groups. A slight increase in intensity of the C=C peak at 1600 cm⁻¹ was also observed on this sample. The increase in intensity of the peak associated with the C-O stretching mode of the vinyl alcohol groups (1085 cm⁻¹) does not appear to be linked to an increase in vinyl alcohol content since the corresponding O-H stretching modes (3350 and 3450 cm⁻¹) did not significantly change in intensity.

On the filled VCE material, gamma irradiation induced a decrease in the intensity of the stretching and bending modes from vinyl acetate groups and of the stretching modes from methylene backbone, consistent with the release of acetic acid and a lowered mobility of the methylene groups (Figure 4). Similar observations were made on thermally-aged VCE samples (Figure 5).

It should be noted that the ATR method measures IR absorption of an evanescent wave in the sample, primarily analyzing the surface chemistry of the sample and minimizing bulk effects.

This may explain why the intensity of some of the effects of radiation and temperature aging are small.

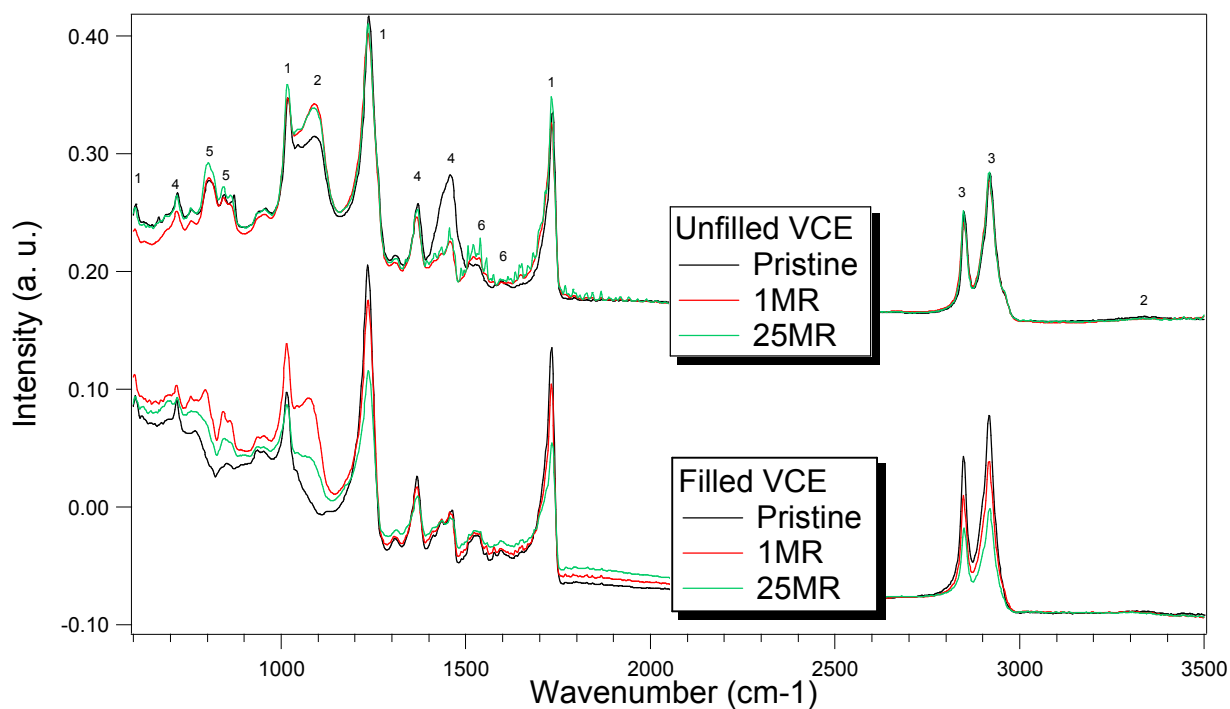


Figure 4. IR spectra of filled and unfilled VCE samples exposed to 0, 1 and 25 MR gamma irradiation.

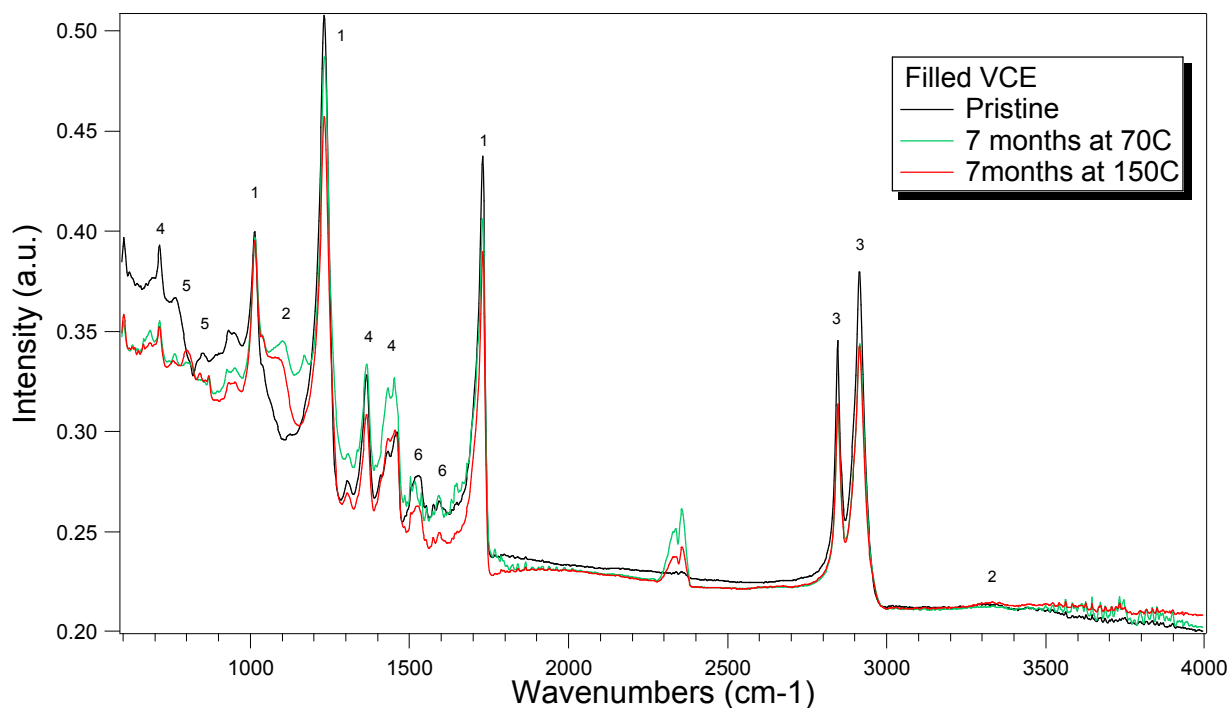


Figure 5. IR spectra of filled VCE samples exposed to temperatures of 20, 70 and 150°C for 7 months, under inert atmosphere.

3.5. Degradation Mechanism

Experimental results described in the FY09 report as well as in the present report show that the VCE terpolymer outgases acetic acid upon gamma irradiation and thermal treatment. This deacetylation was associated with: a loss of mass corresponding to the weight fraction of vinyl acetate in the VCE material, [5] a red shift of the material's visible absorption (an absorption band centered at 375 nm was recorded for thermally-treated VCE), [5] a strongly hindered methylene backbone IR deformation mode for unfilled VCE (a decrease in the intensity of the stretching and bending modes from vinyl acetate groups and of the stretching modes from methylene backbone for filled VCE), and an increase in Yong's modulus. Although the deacetylation mechanism with the lowest activation energy (experimental $E_a \sim 90 \text{ KJ.mol}^{-1}$ for EVA with 33 % VA content) [9] is the simple hydrolysis of the vinyl acetate group (which releases acetic acid while forming a vinyl alcohol group), this mechanism does not account for the observed yellowing of the material nor for the hindered methylene deformation modes. In addition, experiments performed on dry samples maintained in inert conditions showed a release of acetic acid and a yellowing of the material, when only traces of water were available for the hydrolysis reaction. An alternate deacetylation mechanism, with higher activation energy ($E_a \sim 180 \text{ KJ.mol}^{-1}$ for EVA with 33 % VA content), [6] is the process in which a hydrogen atom from the ethylene backbone moves to the acetate group to form acetic acid, inserting a C=C double bond into the backbone of the polymer chain, adjacent to the C atom where the leaving group was formerly attached. When propagating to adjacent vinyl acetate groups, this mechanism releases acetic acid while forming alternating single and double bonds (polyenes, $(-\text{C}=\text{C})_n$) in the polymer backbone. Such a mechanism (see Figure 6) does not require the presence of water and would explain the release of acetic acid, the red-shift in absorption due to polyene formation (polyenes with $n=4-6$ typically generate absorption bands in the 250-400 nm range), [7, 8] the frustrated methylene IR deformation modes due to steric hindrance, as well as the stiffening of the material.

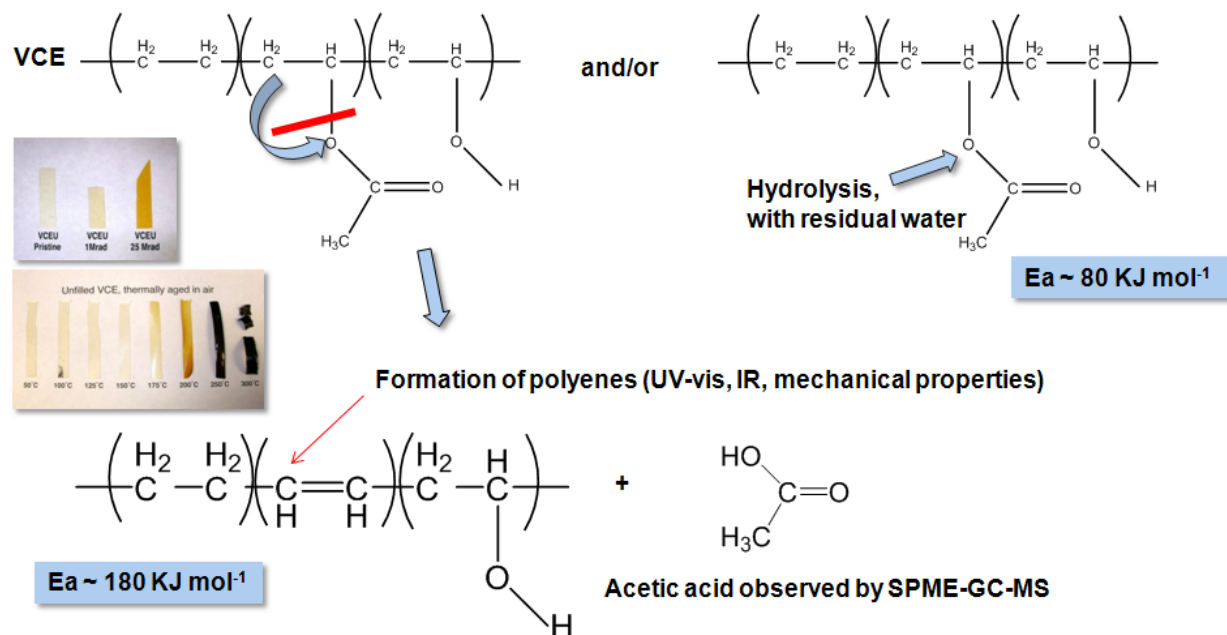


Figure 6. Degradation mechanisms for VCE.

Collaborative work started with Dr. M. Read and Dr. D. Plant from AWE to perform Density Function Theory simulations of the deacetylation reaction and to provide the lowest energy configurations of the VCE terpolymer after removal of the acetate group. Preliminary results predict hindered IR deformation modes on the methylene backbone after addition of the C=C bonds in the background, which is consistent with the experimental IR results obtained on aged VCE samples. Experimental work will also be conducted in collaboration with AWE to detect the C=C double bond formation by NMR spectroscopy.

4. Conclusion

Experiments performed in FY10 included SPME-GC-MS, mechanical testing, toluene swelling and IR spectroscopy on both filled and unfilled VCE materials aged with gamma radiation and thermal treatments.

Experimental results described in the FY09 report, as well as in the present report, show that the VCE terpolymer outgases acetic acid upon gamma irradiation and thermal treatment. This deacetylation was associated with a loss of mass corresponding to the weight fraction of vinyl acetate in the VCE material, a red shift of the material's visible absorption (an absorption band centered at 375 nm was recorded for thermally-treated VCE), a strongly hindered methylene backbone IR deformation mode for unfilled VCE (a decrease in the intensity of the stretching and bending modes from vinyl acetate groups and of the stretching modes from methylene backbone for filled VCE), and an increase in Yong's modulus. A model based on the formation of a C=C bond in the methylene backbone upon abstraction of the acetate group is proposed, which is consistent with the experimental observations.

5. Future work

FY11 will be focused on finalizing a manuscript in collaboration with the AWE group, and on studying various sets of VCE part returns. The parts will have resided in various systems for various periods of time. We will use tensile testing, durometer analysis, Differential Scanning Calorimetry, Toluene Swelling tests, Nuclear Magnetic Resonance, and Infra-Red spectroscopy to analyze the parts and provide information on their aging in actual systems.

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